DIOXIN EMISSION BY INSTALLATIONS FOR CHLORORGANIC COMPOUNDS PRODUCTION IN THE REPUBLIC OF BASHKORTOSTAN, RUSSIA

Faiz Khizbullin, Valery Maystrenko, Ludmila Chernova, Irina Khasanova and Irina Muslimova

Research Institute of Secure Life Activity, 12/1, 8 Marta Str., 450005, Ufa, Bashkortostan, Russia

Introduction

The Republic of Bashkortostan is a region with high concentration of chlororganic chemical plants. The majority of the plants are situated along the Belaja river and they discharge they wastes right into the river and the atmosphere. Pollution of the environment by polychlorinated dioxins (PCDDs) and dibenzofurans (PCDFs) in Bashkortostan was considered at symposiums on dioxins and related compounds[1-3]. Since 1994 monitoring of PCDDs/ PCDFs emission discharged by installations for production of chlororganic compounds has been carried out. It has been stated that installations for vinyl chloride production and liquid and gaseous waste incineration at the Kaustic plant, the city of Sterlitamak, and also installations for 2,4-D amine salt production and chlororganic waste incineration at the Khimprom plant, the city of Ufa.[4-6] are the main sources of dioxin formation.

Materials and Methods

Sampling and sample preparation for analysis were performed in compliance with recommendations of US EPA 1613, as reported[4]. For control of sample preparation process isotope-labelled standards were introduced into all samples. The isotope-labelled standards were used in the form of solution in acetone. Water samples were extracted with three portions of hexane. Hexane extract was purified by silica gel and coal columns. The analysis was performed using a mass-spectrometer Incos 50 equipped with a chromatograph Varian 3400 and a capillary column DB-5MS in the regime of selective ion-determination. The inner isotope-labelled standards were used for calculation of mass-chromatograms. Analysis error was 60%.

Results and Discussion

The process of vinyl chloride production at the Kaustic plant includes two stages: dichloroethane isolation by oxidative chlorination of ethylene and its consequent hydrolysis. Waste water is processed and discharged to biological treatment facilities. Liquid waste is incinerated. Dioxin emission discharged by the incinerator has been evaluated in the operation mode, at the start of operation and during a stop in functioning. Furnace gas and water after furnace gas tower washing have been analysed. Isomer composition of furnace gas samples is given in Table 1. Sample 2 has been taken during the start period. For two hours feedstock delivery has been increased from 30 to 100% and temperature has been raised from 240 to 310^{o}C. One can see from the table that in sam-

ple 2 PCDDs/PCDFs content has been increased up to 7,98 ng/m^3 (TEQ) and relative quantity of hexa-, hepta- and octachlordibenzodioxins – up to 13%, tetra- and pentachlordibenzofurans – up to 19%, whereas the quantity of high-chlorinated dibenzofurans has been reduced to 68%. During sampling No. 4 there has been a short-duration suspension in production process caused by compressor changeover.

Table 1
The PCDDs/PCDFs content in furnace gas discharged by the vinyl chloride industrial waste incinerator, ng/m^3

Isomer	Sample No.				
	1	2	3	4	5
2,3,7,8-TCDD	ND	ND	ND	ND	ND
1,2,3,7,8-PeCDD	ND	ND	ND	ND	ND
HxCDD	ND	4.47	ND	2.36	0.45
HpCDD	0.61	29.69	0.51	27.52	9.70
OCDD	5.50	271.33	8.37	159.39	89.44
2,3,7,8-TCDF	ND	7.51	ND	ND	0.53
PeCDF	ND	15.51	ND	4.86	ND
HxCDF	3.47	37.86	0.66	58.78	17.28
HpCDF	13.66	120.82	4.74	346/73	96.94
OCDF	36.58	441.32	30.18	1461.86	392.54
TEQ	0.53	7.98	0.16	11.72	3.37

At considerable increase of PCDDs/PCDFs content in this sample - up to 11.72 ng/m^3 (TEQ) the isomer ratio relevant to that installation has been preserved. . Alongside with furnace gas there is soot present in all samples in the amount of 0.05 to 0.13%. After furnace gas washing the soot is concentrated in waste water that contains 132.4 ng/l (TEQ) of PCDDs/PCDFs. PCDDs/ PCDFs emission from the chlororganic waste incinerator is 712.16 μg/h (TEQ). Considering that PCDDs/PCDFs content in vinyl chloride does not exceed 2 pg/g (TEQ) the total PCDDs/PCDFs emission is 0.16 g (TEQ) per 10 000 tons of vinyl chloride. Furnace gas contains 0.80% of the total PCDDs/PCDFs amount, waste water – 0.79%, soot – 92.40%, solids – 6.01%. Analysis of the soil sampled near the installation shows that the soil contains from 0.38 to 27.2 ng/kg (TEQ) of PCDDs/PCDFs. Maximum pollution is observed in the south-west direction of the plant what points to dioxins transfer with the wind.

Production of 2,4-D amine salt at the Khimprom plant in Ufa includes two stages – phenol chlorination and 2,4-dichlorphenoxiacetic acid isolation. PCDDs/PCDFs are formed at both stages. Since the beginning of the 90s the technology has been improved what permitted to reduce 2,3,7,8-TCDD content in 2,4-D amine salt. Besides, PCDDs/PCDFs get into the environment with waste water discharged by the chlororganic waste incinerator. The total PCDDs/PCDFs emission is 54 g

(TEQ) per 10 000 tons of 50% herbicide water solution. In this amount 73.50% of PCDDs/PCDFs is in 2,4-D amine salt, 26.33% in waste water, 0.16% in soot and 0.01% in furnace gas (Table 2).
The findings prove that emission of dioxins discharged by the installations for 2,4-D amine salt and vinyl chloride production is variable.
In the process of 2,4-D amine salt production the major portion of PCDDs/PCDFs is getting into the environment through finished product and waste water. Chlororganic waste incinerator produces 0.17-0.20%. In vinyl chloride production in the process of chlororganic waste burning about 89% of the total PCDDs/PCDFs amount is formed. The finished product, waste water and solid waste contain only 11%.

Table 2
PCDDs/ PCDFs (TEQ) emission at 2,4-D amine salt production

Object	PCDDs/ PCDFs content	PCDDs/ PCDFs emission	
		μg/ton	%
2,4-D	3,98 μg/kg	3980,00	73,50
Waste water	0,25 ng/l	1425,60	26,33
Soot	0,79 μg/m^3	8,69	0,16
Furnace gas	0,26 ng/m^3	0,65	0,01

Conclusion

Thus the main methods of reducing PCDDs/PCDFs emission in 2,4-D amine salt production are related to reduction of dioxins quantity in finished product, while in vinyl chloride production the main methods are related to optimisation of the waste incineration process. Special attention should be paid to removal of soot out of waste water that goes to biological water treatment plant. In this process an important role belongs to PCDDs/PCDFs adsorption by solids suspended in water. Pollution is mostly concentrated in the sediment that is discharged to the Belaya River from the water treatment plant. PCDDs/PCDFs content in waste water discharged by the biological treatment facilities is 4-7 pg/l, due to sediment it is increased up to 21 pg/l. Research shows that PCDDs/PCDFs content in discharged waste water can be reduced by additional water purification, removing mud particles. The classical method of waste water treatment at biological water treatment plant does not guarantee proper quality of discharged waste water.

References

1. Fedorov L; *Organohalogen Compounds*. **1992,** 9, 75.
2. Khamitov R and Maystrenko V; *Organohalogen Compounds*. **1995**, 24, 309.
3. Khamitov R, Simonova N, Maksimov G and Maystrenko V; *Organohalogen Compounds*. **1996**, 28, 171.
4. Khizbullin F, Muslymova I, Khasanova I, Chernova L and Abdraschitov Ja; *Organohalogen Compounds*. **1998**, 36, 225.
5. Maystrenko V, Khizbullin F, Khasanova I, Chernova L and Dmitriev Ju; *Organohalogen Compounds*. **1998**, 36, 237.
6. Maystrenko V, Kruglov E, Amirova Z and Khamitov R; *Chemosphere*. **1998**, 37, 1699.